

10/520989

10 Rec'd PCT/PTO 10 JAN 2005

REC'D 26 AUG 2003

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FILING DATE.

APPLICATION NUMBER: 60/395,085

FILING DATE: July 11, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/21871

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7-12-02 603 6085 . 07 11 02
APR

P01072US1A(P309)



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of

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CHRISTINE M. RADEMACHER,
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CERTIFICATE OF MAILING
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EL725988575US - "Express Mail Post Office to
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20231, on July 11, 2002

) Kimberly A. Bright, Secy. to Arthur M. Reginelli

Serial No.

Filed

For PREPARATION OF
FUNCTIONALIZED ANIONIC
POLYMERIZATION INITIATORS

TRANSMITTAL SHEET

Enclosed are the following documents:

Provisional Patent Application (17 pages)
Provisional Application Transmittal Sheet
Patent Application Bibliographic Data Sheet
Return Receipt Postcard

AUTHORIZATION TO CHARGE DEPOSIT ACCOUNT

The Commissioner is hereby authorized to charge payment of any fees
associated with this communication or credit any overpayment to Deposit Account
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PATENT

Docket No

P01072US1A(P309)

Transmittal of Provisional Application Pursuant to 37 C.F.R. § 1.53(c)

Application of Thomas A. Antkowiak, Christine M. Rademacher, Anthony J. Ramic and David F. Lawson

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For Preparation of Functionalized Anionic Polymerization Initiators

Enclosed is a new provisional patent application. It includes 17 pages of text and 0 sheet(s) of drawings.

1. Enclosed is an application assignment to Bridgestone Corp. and a completed Assignment Recordation Cover Sheet.
2. Enclosed is Patent Application Bibliographic Data Sheet.
3. The USPTO is authorized to charge the fee pursuant to 37 C.F.R. § 1.16(k) (\$160.00) to Deposit Account No. 06-0925. Also, during the pendency of this application, please charge any fees incurred and credit any overpayments made to that same Deposit Account.
4. Kindly address all correspondence relating to this application to the following address:

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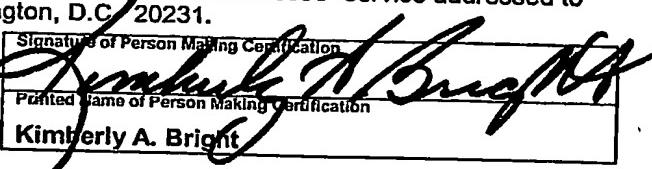
Registration Number 40,139	Telephone Number 330/376-1242
Date July 11, 2002	

Signature 
Title Name Arthur M. Reginelli

Certificate of Express Mailing

- Under 37 C.F.R. § 1.10, I certify that this application is being deposited, on the date indicated below, with the United States Postal Service "Express Mail Post Office to Addressee" service addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Express Mail Mailing Label No. EL725988575US
Date of Deposit July 11, 2002
AppTr-Provisional (Oct-00)

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APPLICATION INFORMATION

Title Line One:: PREPARATION OF FUNCTIONALIZED ANIONIC PO
Title Line Two:: LYMERIZATION INITIATORS
Total Drawing Sheets:: 0
Formal Drawings?:: No
Application Type:: Provisional
Docket Number:: P01072US1A
Secrecy Order in Parent Appl.?:: No

REPRESENTATIVE INFORMATION

Registration Number One:: 29393
Registration Number Two:: 47839
Registration Number Three:: 34031
Registration Number Four:: 40139
Registration Number Five:: 27182

Source:: PrintEFS Version 1.0.1

PREPARATION OF FUNCTIONALIZED ANIONIC POLYMERIZATION INITIATORS

FIELD OF THE INVENTION

5 This invention relates to novel processes for preparing functionalized lithium compounds that are useful as initiators for anionic polymerizations.

BACKGROUND OF THE INVENTION

10 Conjugated diene monomers are often anionically polymerized by using alkylolithium compounds as initiators. Selection of certain alkylolithium compounds can provide a polymer product having a functionality at the head of the polymer chain. The ability to head-functionalize anionically-polymerized polymers has provided many advantages to tire technology. For example, lithiated cyclic amines, such as lithio hexamethyleneimine, has been employed to initiate 15 the polymerization of conjugated dienes, as well as the copolymerization of conjugated dienes and vinyl aromatic monomers, to produce polymers having a cyclic-amine head functionality. These polymers have proven to provide technologically useful tire treads that are characterized by improved traction, low rolling resistance, and improved wear.

20 The synthesis of these polymers is advantageously conducted in environmentally friendly solvents such as technical hexanes by using continuous polymerization techniques. The high temperatures at which these polymerizations occur, however, has led to the problem of reduced head functionality. To alleviate this problem, it was discovered that the use of cyclic aminoalkylolithium 25 compounds, such as hexamethyleneimine propyllithium, could withstand high polymerization temperatures and thereby lead to polymers having greater functionality.

30 The preparation of these cyclic aminoalkylolithium compounds, however, has proven to be difficult and inefficient. In one technique, the initiators are prepared by reacting a cyclic aminoalkylolithium halide with elemental lithium or an organolithium compound. Where the halide is reacted with elemental lithium, the product must be separated from byproducts such as lithium metal and

lithium chloride mud. Separation of these products can prove difficult, in part due to the limited solubility of the aminoalkyllithiums. Additionally, the product made by this route is often contaminated with undesirable side products such as the products of Wurtz coupling. Moreover, the precursor aminoalkylhalide compounds
5 are unstable since they are capable of self-quaternization. As a result, it is necessary to store these compounds at low temperatures or as their hydrohalide salts and liberate the aminoalkylhalide by treatment with base a short time before lithiation is carried out. When the halide is reacted with an organolithium compound, the reaction inefficiently requires two or more equivalents of lithium
10 from the organolithium to prevent undesirable side reactions that occur between the lithiated amine and the resultant chlorinated organic byproducts.

Because cyclic aminoalkyllithium compounds remain useful as initiators for preparing functionalized polymers, there is a need to overcome the problems associated with the synthesis of these initiators.

15

SUMMARY OF THE INVENTION

In general the present invention provides a process for preparing a cyclic-aminoalkyllithium anionic polymerization initiator, the process comprising combining a cyclic-amino functionalized styryl compound and an organolithium
20 compound.

The discovery that aminoalkyllithium initiators can be prepared by reacting an organolithium compound with certain functionalized styryl derivatives provides a method that overcomes the problems associated with the prior art. Advantageously, this lithiation proceeds by way of an addition reaction, which
25 thereby avoids by-products that result from substitution reactions of the halo alkyl precursors with lithium or lithium-containing compounds and avoids the need to liberate or treat the quaternized base. Further, because the addition reaction to the functionalized styryl derivatives occurs between the amine and phenyl substituents of the styryl derivative, the reaction proceeds rapidly and provides a
30 highly stabilized carbon-lithium site. Also, where the functionalized styryl derivative is prepared by a substitution reaction in lieu of an addition reaction, the process has been found to be more efficacious because less starting material is lost to the formation of undesirable side-products. The resultant aminoalkyllithium

initiators can advantageously be used to prepare polymers that include a cyclic amine functionality at the head of the polymer.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

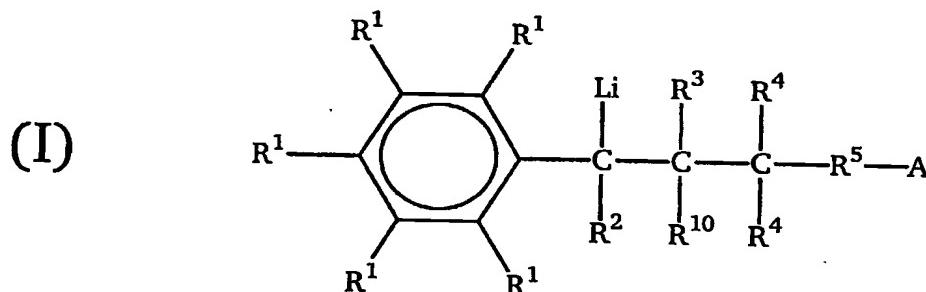
5 I. General

The process of this invention combines a functionalized styryl reagent with an organolithium reagent to form a functionalized lithium-containing anionic polymerization initiator.

10 II. Reaction Between Functionalized Styryl Compound & Organolithium

A. General

The combination of the functionalized styryl reagent and the organolithium reagent is believed to provide an initiator that can be represented by the formula I



where each R^1 is independently hydrogen or a monovalent organic group, R^2 is hydrogen or a monovalent organic group, R^3 is hydrogen or a monovalent organic group, each R^4 is independently hydrogen or a monovalent organic group, R^5 is a covalent bond or a divalent organic group, R^{10} is the organic substituent or residue that derives from the organolithium reagent (R^{10}Li), and A is a functional group that will react or interact with rubber fillers or otherwise have a desirable impact on a filled rubber composition or vulcanizate.

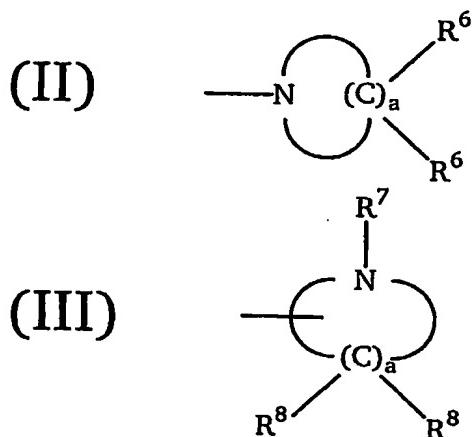
Functional groups that will react or interact with rubber fillers include strong, weak, or selective functional groups. Strong functional groups

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include those substituents that undergo some type of bonding with the filler, e.g., covalent or ionic bonding. Weak functional groups include those groups that interact with filler via through-space interaction, e.g., H-bonding or van der Waals interaction, as well as those groups that interact or attract to each other and thereby form a domain within the rubber matrix of the polymer. Selective functional groups include those groups whose affinity toward filler particles or rubber can be activated after processing, e.g., during cure. Examples of selective functional groups include those described in co-pending U.S. Serial No. 10/020,666, which is incorporated herein by reference.

Useful functional groups A include amine-containing substituents, alkyltin substituents, short-chain thermoplastic polymer segments, polynuclear aromatic groups, polyalkylene oxides, protected alcohols, and protected mercaptans.

Preferred functional groups A include cyclic amine-containing substituents that may be defined by the formulae II or III:



where each R⁶ is independently hydrogen or a monovalent organic group, R⁷ is a monovalent organic group, a bridging bond, or a divalent organic group, each R⁸ is independently hydrogen, a monovalent organic group, a bridging bond, or a divalent organic group, and a is an integer from 4 to about 20.

The monovalent organic groups are preferably hydrocarbyl groups such as, but not limited to alkyl, cycloalkyl, substituted cycloalkyl, alkenyl,

cycloalkenyl, substituted cycloalkenyl, aryl, allyl, substituted aryl, aralkyl, alkaryl, and alkynyl groups, with each group preferably containing from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group, up to 20 carbon atoms. These hydrocarbyl groups may contain heteroatoms such as, but 5 not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms.

The divalent organic groups are preferably hydrocarbylene groups such as, but not limited to, alkylene, cycloalkylene, substituted alkylene, substituted cycloalkylene, alkenylene, cycloalkenylene, substituted alkenylene, substituted cycloalkenylene, arylene, and substituted arylene groups, with each 10 group preferably containing from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group, up to 20 carbon atoms. These hydrocarbylene groups may contain heteroatoms such as, but not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms.

The substituents represented by formula I can include multi-cyclo 15 substituents such as bicyclo and tricyclo substituents. These multi-cyclo substituents are represented by formula I where R⁷ and R⁸ combine, either by a direct bond, *i.e.*, a bridging bond, or via a divalent substituent, or by combining each R⁸ via a divalent substituent.

B. Amount of Reactants

20 The functionalized styryl reagent and the organolithium can be reacted in a 1:1 molar ratio, although an excess of either reagent can be employed. In a preferred embodiment, an excess of the organolithium is employed (*e.g.*, 1 mole of organolithium to 0.9 moles of the functionalized styryl).

C. Reaction Medium

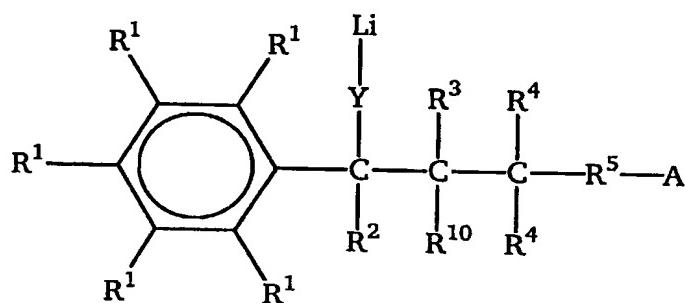
25 This reaction can take place by contacting the functionalized styryl and the organolithium under ambient conditions within an inert solvent. This reaction can also take place in the presence of monomer. In one embodiment, the initiator is prepared *in situ* whereby the reaction between the functionalized styryl and the organolithium compound occurs in the presence of monomer that is 30 intended to form the main chain of the resultant polymer.

D. Chain Extension

In another embodiment, the initiator is prepared in the presence of a small amount of monomer, (e.g., from about 2 to about 30 moles of monomer/mmol of lithium) outside the presence of the majority of the monomer to be polymerized; i.e., monomer other than that which is intended to form the main chain of the resultant polymer. Or, the monomer is added a very short time after the organolithium reagent is added to the functionalized styryl compound. In this embodiment, the resultant initiator will include a chain-extended substituent. This initiator can be represented by the formula IV

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(IV)



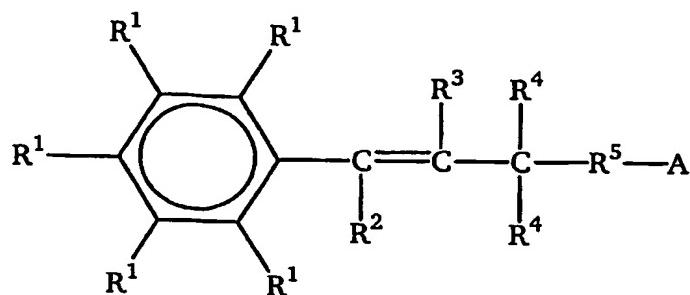
where each R¹, R², R³, each R⁴, R⁵, R¹⁰, and A are as defined as above, and Y represents a chain-extended segment that results from the polymerization of the small amount of monomer present during the formation of the initiator. In preferred embodiments, the segment Y will include from about 3 to about 20 units deriving from the monomer.

III. Functionalized Styryl Compound

20 **A. Structure**

The functionalized styryl reagent may be represented by the formula V:

(V)



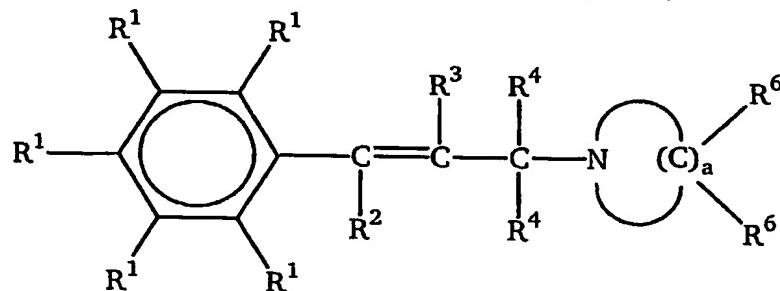
where each R¹, R², R³, each R⁴, R⁵, and A are as defined above.

5

B. Preferred Examples

In one embodiment, the preferred functionalized styryl reagent is a cyclic-amino functionalized styryl reagent, which can be defined by the formula VI:

(VI)



10

where R¹, R², R³, R⁴, R⁶, and a are defined above. Preferably, each R¹ is a hydrogen atom or an alkyl group including 1 to about 6 carbon atoms, R² is a hydrogen atom, an alkyl group containing 1 to about 6 carbon atoms, or a phenyl group, R³ is a alkyl group containing 1 to about 6 carbon atoms, each R⁴ is a hydrogen atom or an alkyl group containing 1 to about 6 carbon atoms, each R⁶ is hydrogen or an alkyl group including about 1 to about 6 carbon atoms, and a is an integer from about 4 to about 12.

15

1. Specific Examples

Some specific examples of the cyclic-amino functionalized styryl compounds include N-(cinnamyl)-pyrrolidine, -3-methylpyrrolidine, -3,4-

20

dimethylpyrrolidine, -3,3-dimethylpyrrolidine, -piperidine, -4-methylpiperidine,
-3-methylpiperidine, -morpholine, -4-methylpiperazine, -4-ethyl-piperazine, -4-
propylpiperazine, -hexamethyleneimine (or -perhydroazepine),
-trimethylperhydroazepine, -azacyclotridecane, -azacyclohexadecane,
5 -azacycloheptadecene, -trimethylazabicyclooctane, -perhydroisoquinoline, and
-perhydroindole.

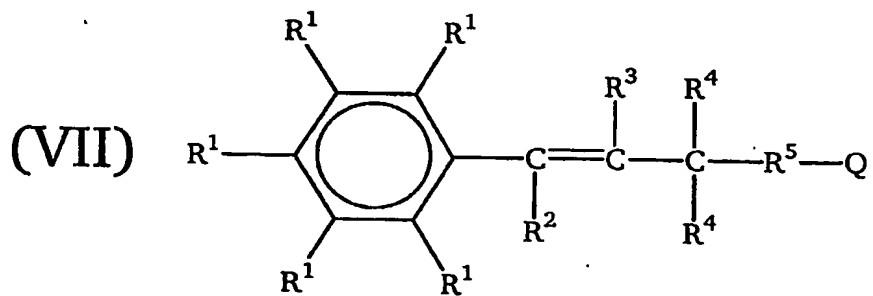
C. Preparation

1. Preferred Cyclic-Amino Functionalized Styryl Compound

10 a. General

In one embodiment, the preferred cyclic-amino functionalized styryl reagent can be prepared by reacting a reactive styryl reagent with a cyclic amine via substitution of an allylic halide or coupling of an allylic alcohol. For example, a styryl amino compound can be formed by the reaction of a cyclic secondary amine with cinnamyl alcohol in the presence of tin dichloride and a palladium(0) catalyst. Styryl amino compounds can also be formed via the displacement of halogen from a cinnamyl halide that is treated with a secondary cyclic amine. An excess of the same amine, another amine, or another base can be used as a proton scavenger. The reactive styryl reagent can be defined by formula VII:

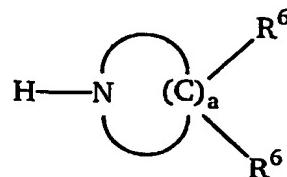
20



where each R¹, R², R³, each R⁴, and R⁵ are defined as above, and Q is a leaving group. Exemplary leaving groups include halides, ester groups, alkyl or aryl sulfonates, and carboxylates.

The cyclic amine can be defined by the formula VIII:

(VIII)



where each R^6 and a are defined as above. Useful cyclic amines include
5 pyrrolidine, piperidine, 3-methylpiperidine, 4-alkylpiperazine such as 4-propylpiperazine, perhydroazepine, which is also known as hexamethyleneimine,
1-azacyclooctane, perhydroisoquinoline, or perhydroindole.

It is believed that the cyclic amine will displace the leaving group,
and the nitrogen atom will bond with or via R^5 in a nucleophilic substitution
10 reaction.

b. Reactant Amounts

The preparation of the cyclic-amino functionalized styryl reagent can
be carried out by reacting one mole of the reactive styryl reagent with one mole of
the cyclic amine and one mole of a scavenging or non-nucleophilic base. Those
15 skilled in the art will appreciate that the cyclic amine can act as the scavenging or
non-nucleophilic base, and therefore two moles of the cyclic amine should be
employed per mole of the reactive styryl compound in the situation where a
separate base is not employed. As in other embodiments, an excess of any of the
reactants may be employed, although an excess of cinnamyl halide is not
20 recommended.

2. Other Embodiments

a. General

In other embodiments, the functionalized styryl reagent can be
prepared by reacting a reactive styryl reagent with a nucleophile that is not
25 reactive toward or less reactive toward the active double bond (i.e., won't add to
the double bond) of the reactive styryl reagent than toward the carbon bearing the
leaving group of the reactive styryl reagent. As with the previous embodiments,

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this functionalized styryl reagent is then reacted with an organolithium reagent to form a functionalized lithium containing anionic polymerization initiator.

For example, the reactive styryl reagent can be reacted with a polymer having an -OLi group at its tail to form a functionalized styryl reagent.

5 Those skilled in the art appreciate that a polymer having an -OLi at its tail can be prepared by terminating a living polymer with an epoxide. Where the living polymer is initiated with a functionalized initiator such as a cyclic amine or a cyclic amino lithium or a trialkyltin lithium, the resulting functionalized styryl reagent will include the cyclic amino or trialkyltin group as a functional group.

10 **III. Organolithium Compounds**

Useful organolithium reagents can be defined by the formula $R^{10}Li$, where R^{10} is a monovalent organic group as defined above, with hydrocarbyl groups being preferred. The preferred hydrocarbyl groups are alkyl groups containing 1 to about 6 carbon atoms. The preferred organolithium compound is 15 *n*-butyl, which is commercially available from Chemetall Foote Corporation or FMC Corp. Lithium Division.

V. Polymerization

A. General

20 Polymerizations that employ the initiator prepared according to this invention may be employed within batch processes, continuous processes, metered batch processes or semi-continuous processes. The preferred polymerization methods employ the chain extended initiator inasmuch as the stability and solubility of the initiator are increased when chain extended. Polymerization is 25 conducted in an anhydrous polar or non-polar solvent, such as tetrahydrofuran (THF), a hydrocarbon solvent, such as the various cyclic and acyclic hexanes, heptanes, octanes, pentanes, their alkylated derivatives, and mixtures thereof. The polymerization is preferably conducted in the absence of air.

B. Monomers

30 The initiators prepared according to the present invention can be employed to polymerize any monomer that can be anionically polymerized. Useful monomers include conjugated diene monomers such as, but not limited to, 1,3-

butadiene, 2,3-dimethyl-1,3-butadiene, 2-phenyl- 1,3-butadiene, isoprene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, and 4,5-diethyl-1,3-octadiene. In one embodiment, the conjugated diene monomer are copolymerized with vinyl-substituted aromatic monomers such as, but not limited
5 to, styrene , 4-methylstyrene, α -methylstyrene, 3,5-diethylstyrene, 4-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 2,3,4,5-tetraethylstyrene, 3-methyl-5-normal-hexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 3,5-diphenylstyrene, 1-vinylnaphthalene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene,
10 and the like, and mixtures thereof.

1. Randomizers

In order to promote randomization in copolymerization and to control vinyl content, a polar coordinator may be added to the polymerization ingredients. Amounts range between 0 and 90 or more equivalents per equivalent
15 of lithium. The amount depends on the amount of vinyl desired, the level of styrene employed and the temperature of the polymerization, as well as the nature of the specific polar coordinator (modifier) employed. Suitable polymerization modifiers include, for example, ethers or amines to provide the desired microstructure and randomization of the comonomer units.
20

Other compounds useful as polar coordinators are organic and include tetrahydrofuran (THF), linear and cyclic oligomeric oxolanyl alkanes such as 2,2-bis(2'-tetrahydrofuryl) propane, di-piperidyl ethane, dipiperidyl methane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, dimethyl ether, diethyl ether, tributylamine and the like. The linear and cyclic oligomeric
25 oxolanyl alkane modifiers are described in U.S. Pat. No. 4,429,091, owned by the Assignee of record, the subject matter of which relating to such modifiers is incorporated herein by reference. Compounds useful as polar coordinators include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons. Other examples include dialkyl ethers of mono and oligo alkylene
30 glycols; "crown" ethers; tertiary amines such as tetramethylethylene diamine (TMEDA); linear THF oligomers; and the like.

The amount of initiator employed in conducting anionic polymerizations can vary widely based upon the desired polymer characteristics. In one embodiment, it is preferred to employ from about 0.1 to about 100, and more preferably from about 0.33 to about 10 mmol of lithium per 100 g of monomer.

5

C. Termination

The anionic polymerizations can be quenched by employing several techniques that are well known in the art. In one technique, a terminator is added that may impart a functionality to the tail end of the polymer or that may serve as 10. a coupling agent. Suitable terminators include, but are not limited to, metal halides, organic halides, alcohols, carboxylic acids, inorganic acids, sulfonic acid, water, and mixtures thereof. Some specific examples of preferred terminators include tin tetrachloride, tributyl tin chloride, silicon tetrachloride, trioctyl tin chloride, dioctyl tin dichloride, carbon dioxide, and epoxides.

15

D. Polymer Characteristics

The characteristics of the resultant polymer can vary greatly by employing techniques that are well known in the art. The molecular weight of the polymer ("base polymer") that is produced in this invention is optimally such that a proton-quenched sample will exhibit a gum Mooney (ML₁₊₄@100°C) of from 20. about 1 to about 150. In a preferred embodiment, the uncoupled polymer will have a number average molecular weight of from about 5,000,000 to about 1,000,000, and preferably from about 50,000 to about 300,000 as measured by using gel permeation chromatography (GPC) calibrated with polystyrene standards and adjusted for the Mark-Houwink constants for the polymer in question. The 25. molecular weight distribution of the polymer is preferably less than 2, more preferably less than 1.5, and even more preferably less than 1.3.

30

In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

EXAMPLES**Example 1**Preparation of Cinnamyl-HMI

To a solution of hexamethyleneimine (HMI) (31 g, 0.3 mol) in cyclohexane, cinnamyl chloride (22.9 g, 0.15 mol) was added dropwise at room temperature with stirring. After 24 hours of agitation at 65°C, the amine chloride salt was filtered off and the resulting solution (cyclic-amino functionalized styryl compound) concentrated to a dark yellow oil. The product was purified by vacuum distillation (~1 mm Hg, 80°C) to yield 22 g (68% yield). The structure was confirmed by ^1H NMR analysis.

Preparation of Initiator

The BuLi-cinnamyl HMI initiator (chain extended) was prepared just prior to polymerization. A small amount of hexanes (61.6 g) was charged to a nitrogen purged reactor. Butyllithium (1.6 M, 8.5 mL) was added followed by cinnamyl-HMI (4.49 M, 2.73 mL) prepared above. Butadiene monomer (21.8% in hexanes, 23.4 g), which was used for chain extension, and a polar modifier (1.6 M, 1.02 mL) were charged last. This mixture was allowed to react with agitation at 50°C for 1 hour and then used directly in the polymerization.

20

Reactor Batch Polymerization

The initiator prepared above was employed to polymerize poly(styrene-co-butadiene) in a batch polymerization. Specifically, a 5-Gallon reactor was charged with hexanes (5.95 lbs.), styrene (34% in hexanes, 3.11 lbs.), butadiene (21.8% in hexanes, 15.72 lbs.), and the BuLi-cinnamyl HMI initiator prepared above (13.6 mmol C-Li) were charged and the reactor was heated in batch mode to 50°C and temperature peaked at 60°C, the mixture was stirred an additional 45 minutes and coupled with equal parts of tributyl tin chloride and tin tetrachloride. The resulting polymer was coagulated in isopropyl alcohol, antioxidant, drum-dried, and analyzed. The resultant polymer was analyzed for amine content and showed greater than 80% bound cyclic amine.

Reactor Semi-Batch Polymerization

The initiator prepared above was also employed in a semi-batch polymerization. A 5-gallon reactor was charged with hexanes (6.59 lbs.) and butyllithium-cinnamyl HMI initiator (13.6 mmol C-Li), which was prepared in a similar fashion to that described above. A mixture of styrene (34% in hexanes, 4.77 lbs.) and butadiene (21.87%, 13.42 lbs.) was added over a two-hour period to the 5-gallon reactor. The resulting cement was coupled with equal parts of tributyl tin chloride and tin tetrachloride as above and the final polymer analyzed. The resultant polymer was analyzed for amine content and showed greater than 80% bound cyclic amine.

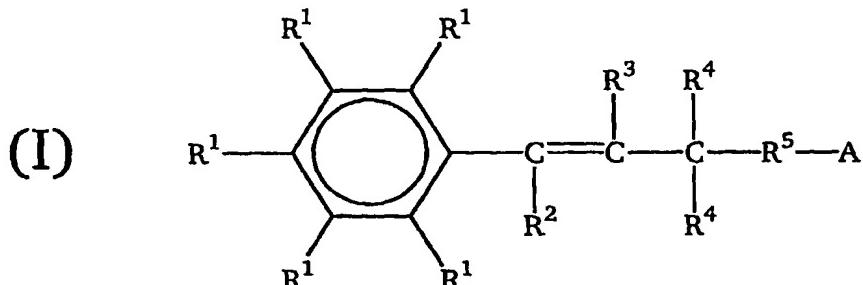
Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

CLAIMS

What is claimed is:

1. A process for preparing a cyclic-aminoalkyllithium anionic polymerization initiator, the process comprising:
5 combining a cyclic-amino functionalized styryl compound and an organolithium compound.

2. The process of claim 1, where the cyclic-amino functionalized styryl compound is defined by the formula I



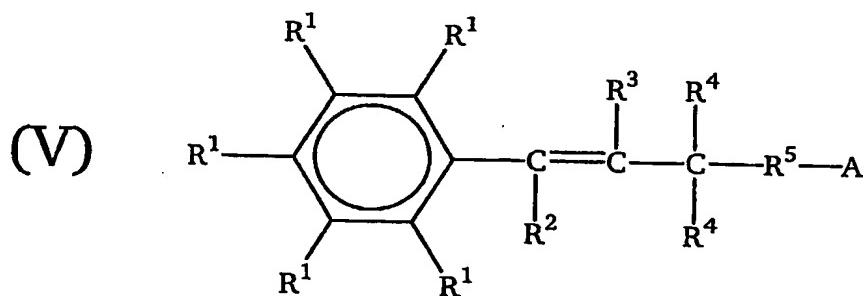
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- where each R¹ is independently hydrogen or a monovalent organic group, R² is hydrogen or a monovalent organic group, R³ is hydrogen or a monovalent organic group, each R⁴ is independently hydrogen or a monovalent organic group, R⁵ is a covalent bond or a divalent organic group, and A is a functional group that will react or interact with rubber fillers or otherwise have a desirable impact on a filled rubber composition or vulcanizate.

3. The process of claim 2, where the cyclic-amino functionalized styryl compound is N-(cinnamyl): -pyrrolidine, -3-methylpyrrolidine, -3,4-dimethylpyrrolidine, -3,3-dimethylpyrrolidine, -piperidine, -4-methylpiperidine, -3-methylpiperidine, -morpholine, -4-methylpiperazine, -4-ethyl-piperazine, -4-propylpiperazine, -hexamethyleneimine (or -perhydroazepine), -trimethylperhydroazepine, -azacyclotridecane, -azacyclohexadecane, 25 -azacycloheptadecene, -trimethylazabicyclooctane, or -perhydroisoquinoline, -perhydroindole.

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4. The process of claim 1, where the organolithium compound is defined by the formula RLi, where R is a monovalent organic group.
5. The process of claim 4, where the organolithium compound is n-butyllithium.
6. The process of claim 1, where the cyclic-amino functionalized styryl compound is prepared by combining a reactive styryl compound and a cyclic amine compound.
- 10
7. The process of claim 6, where the reactive styryl compound is defined by the formula V

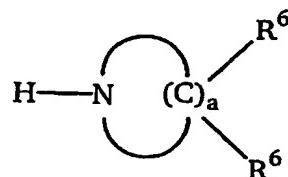


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where each R¹ is independently hydrogen or a monovalent organic group, R² is hydrogen or a monovalent organic group, R³ is hydrogen or a monovalent organic group, each R⁴ is independently hydrogen or a monovalent organic group, R⁵ is a covalent bond or a divalent organic group, and A is a leaving group.

- 20
8. The process of claim 6, where the cyclic amine compound is defined by the formula VI

(VI)



where each R⁶ is independently hydrogen or a monovalent organic group.

- 5 9. The process of claim 8, where the cyclic amine compound is pyrrolidine, piperidine, 3-methylpiperidine, 4-propylpiperazine, hexamethyleneimine, 1-azacyclooctane, perhydroisoquinoline, or perhydroindole.
- 10 10. The process of claim 1, where said step of combining combines about 0.8 mmol of the cyclic-amino functionalized styryl compound with about 1.0 mmol of the organolithium compound.
- 15 11. The process of claim 6, where said step of combining combines about 1.0 mmol of the reactive styryl compound with about 2.0 mmol of the cyclic amine.
- 20 12. The process of claim 10, where step of combining occurs in the presence of about 1 to about 20 mmol of monomer in order to chain extend the initiator.
- 25 13. The process of claim 10, where said step of combining is immediately followed by the addition of 1 to about 20 mmol of monomer for chain extension.
14. The process of claim 1, further comprising the step of combining monomer after said step of combining a cyclic-amino functionalized styryl compound and an organolithium compound.